

Suppression of spin-state transition in epitaxially strained LaCoO_3

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Epitaxial thin films of LaCoO_3 (E-LCO) exhibit ferromagnetic order with a transition temperature $T_C = 85$ K, while polycrystalline thin LaCoO_3 films (P-LCO) remain paramagnetic. The temperature-dependent spin-state structure for both E-LCO and P-LCO was studied by x-ray absorption spectroscopy at the Co $L_{2,3}$ and O K edges. Considerable spectral redistributions over temperature are observed for P-LCO. The spectra for E-LCO, on the other hand, do not show any significant changes for temperatures between 30 K and 450 K at both edges, indicating that the spin state remains constant and that the epitaxial strain inhibits any population of the low-spin ($S = 0$) state with decreasing temperature. This observation identifies an important prerequisite for ferromagnetism in E-LCO thin films.

I. INTRODUCTION

The great variety of mutually competing phases in the cobaltates, caused by the large number of interactions occurring on similar energy scales (e.g., Hund's coupling, crystal field, double exchange, and correlation) has been attracting intense interest for decades. Despite such efforts, many of their aspects continue to stir discussion and to spawn further, more detailed studies (see for instance Ref.s [1, 2, 3, 4, 5, 6, 7, 8]). To a certain degree, cobaltates may appear similar to the manganites — concerning structural aspects, for instance, or the partial occupation of the $3d$ shell —, yet the fact that two or even three different spin states are so closely spaced in energy that they are almost degenerate in many situations gives them their own distinct flavor and causes intriguing physical properties: Bulk LaCoO_3 , for instance, is a nonmagnetic semiconductor at low temperature, $T \leq 35$ K, with the Co^{3+} ions in a low-spin (LS) configuration ($t_{2g}^6 e_g^0$, $S=0$). A transition of all Co^{3+} ions to a high-spin state (HS, $t_{2g}^4 e_g^2$, $S=2$) occurs at about 500 K and is concurrent to an insulator-metal transition. In the temperature range $35 \text{ K} < T < 100 \text{ K}$ where the susceptibility has a broad maximum no consensus seems to have been reached yet: many authors [1, 6, 8, 9, 10, 11] interpret their experimental results in terms of an intermediate-spin state (IS, $t_{2g}^5 e_g^1$, $S=1$) as suggested by an LDA+U calculation [12] (using the local density approximation, LDA, with on-site Hubbard-like correlation effects added), while other groups understand the spin-state transition in this region as a gradual population of higher spin states starting from LS [13, 14, 15, 16]. In Ref. [16], a configuration-interaction CI cluster-model calculation including the full atomic multiplet theory and hybridization effects with the O $2p$ orbitals is used to explain their Co $L_{2,3}$ x-ray absorption and x-ray magnetic dichroism results; there is also good agreement with susceptibility data. The authors do not find an IS contribution in their calculations. Generally accepted is, however, that crossovers between spin states occur in LaCoO_3 upon changing the temperature. They

are caused by the delicate balance between the crystal-field splitting Δ_{CF} and the exchange interaction J_{ex} due to the Hund's rule coupling, inducing a redistribution of electrons on the t_{2g} and e_g levels. Since Δ_{CF} is obviously very susceptible to the Co-O bond length, the balance between Δ_{CF} and J_{ex} can easily be tipped to either side by doping or pressure.

In a previous work [17] it was reported that in contrast to bulk material, epitaxial thin films of LaCoO_3 (E-LCO) become ferromagnetic below the Curie temperature $T_C = 85$ K when grown on $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT) substrates, while polycrystalline thin films (P-LCO) grown under similar conditions do not show any ferromagnetism down to $T \approx 5$ K. The magnetic behavior of the films has been explained in terms of strain effects [18]. In order to directly identify such effects and, thus, to shed light on the mechanism leading to these intriguing magnetic properties, near edge x-ray absorption fine structure (NEXAFS) measurements have been performed at the Co $L_{2,3}$ and the O K edges. These measurements benefit, on one hand, from the sensitivity of the Co $L_{2,3}$ edge on the valence and the spin state of the Co ion, and, on the other hand, from the fact that the unoccupied density of states (DOS) at the O K edge contains information about precisely those orbitals involved in the chemical bonding. Our results show that the spin state is frozen in the E-LCO films while in the P-LCO films there are spectral changes similar to those seen in bulk LCO.

II. EXPERIMENTAL

E-LCO and P-LCO films were grown on $\langle 001 \rangle$ oriented LSAT substrates with a film thickness of about 100 nm by pulsed laser deposition using stoichiometric sinter targets of the corresponding compound. To ensure clean sample surfaces the samples were grown *in-situ* prior to measurements. The growth conditions were the same as those reported in Ref. [17]. For the preparation of the P-LCO films the LSAT substrates were covered with a 20 nm thick polycrystalline CeO_2 inhibit layer followed

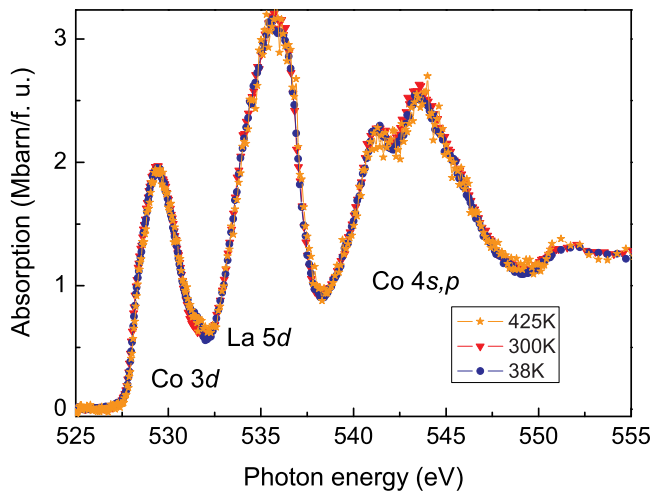


Figure 1: (color online) O 1s x-ray absorption spectra of an epitaxial thin film of LaCoO_3 taken at different temperatures. Over the whole recorded temperature range there is no change in the spectral weight distribution.

by the growth of the LCO film with the same parameters as for the E-LCO films. The samples were characterized by x-ray diffraction and Rutherford backscattering spectrometry; details can be found in Refs. [17, 18]. The NEXAFS measurements were performed at the Institut für Festkörperphysik beamline WERA at the ANKA synchrotron light source (Karlsruhe, Germany). The energy resolution was set to 0.3 eV for the Co $L_{2,3}$ edge and to 0.2 eV for the O K edge. The Co $L_{2,3}$ spectra were collected in the total electron yield (TEY) mode with a probing depth of ≈ 50 Å, while the O K edge spectra were recorded in the fluorescence yield (FY) mode which probes a larger fraction, roughly 700 Å, of the film thickness. Self-absorption and saturation effects in FY mode were corrected. Some Co $L_{2,3}$ spectra were also taken in Auger electron yield (AEY) mode, which is considerably more surface-sensitive than TEY and probes, in this case, about 14 Å deep [19, 20]. Comparison with TEY spectra should clearly bring out contributions, if present, from possible surface effects like reconstruction, contamination, or off-stoichiometry. However, the spectra measured with TEY and AEY were always identical, indicating that surface effects do not play a significant role in these compounds when prepared and examined under these conditions. Photon energy calibration was ensured by simultaneously measuring the O K and the Ni L_3 peak positions of a NiO single crystal and comparing them with literature [21].

III. RESULTS AND DISCUSSION

In NEXAFS, electrons from core levels are excited into unoccupied states above the Fermi level. In the case of

the O K edge transitions of O 1s electrons to the unoccupied O 2p states hybridized with Co 3d, La 5d, and Co 4s,p states are studied. Specific peaks and features of the O K edge spectrum can be assigned to these hybrid states [22], cf. also Fig. 1. An interpretation of these absorption spectra as a partial unoccupied density of states (DOS) is possible, mainly because the screening is good and minimizes effects of the 1s core hole [23]. If, on the other hand, the overlap of the core hole with the final states is significant and the screening is weak, as is the case for the 2p core hole in the Co $L_{2,3}$ edge transition, the shape of the spectra is reduced to a single spin-orbit split “white line” and is governed by atomic-like multiplet effects. For their interpretation crystal field and charge transfer effects have to be taken into account [24].

A. O K edge

Fig. 1 shows the results of temperature-dependent O 1s NEXAFS for the E-LCO film. Over the whole energy range and for all applied temperatures the spectral shape clearly does not change for this sample. We will now focus on the energy region around 529 eV (“pre-peak” region) since it reflects the O 2p orbitals hybridized with Co 3d orbitals of t_{2g} and e_g character. Their centers of gravity are offset in energy by slightly less than 1 eV, consistent with Ref. [1]. This region is shown in more detail in Fig. 2. The pre-peak intensity is, hence, essentially proportional to the number of holes in t_{2g} - and e_g -derived states.

The spectra of the P-LCO film exhibit clear evidence

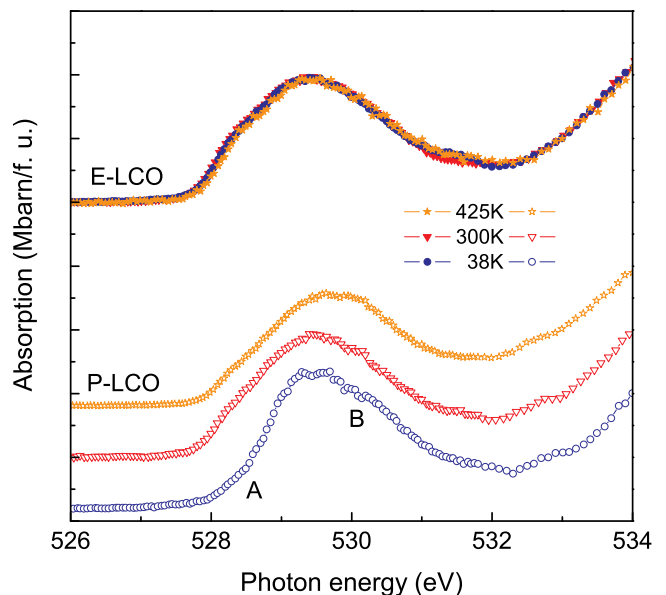


Figure 2: (color online) The O K low-energy region for the E-LCO and the P-LCO thin films. Open symbols: P-LCO film. (The traces for different temperatures are offset for clarity.) Full symbols: E-LCO film strained by the substrate.

for a (partial) rearrangement of the electrons with temperature between the different $O2p$ - $Co3d$ states: For 38 K, the t_{2g} -derived spectral weight (Region A in Fig. 2) is very low, indicating a high electron filling of the corresponding levels. At room temperature and above [33], a significant amount of spectral weight has shifted from the “ e_g area” (Region B) to the “ t_{2g} area” (Region A). This type of rearrangement is clearly consistent with a contribution of higher spin states that increases with temperature at the expense of the LS state predominant at low temperatures. In other words, the Co ions are undergoing a spin-state transition similar to the situation for bulk LCO. We find it interesting to note that a recent first-principles calculation [25] predicts such a rearrangement with energy shift only if the higher spin state is HS; if it is IS no energy shift compared to LS seems to be involved.

The behavior of the epitaxial film, E-LCO, is entirely different. The spectra for the whole temperature range are almost point-per-point equivalent; the spectral shape even for $T \approx 40$ K resembles closely the spectrum for the polycrystalline film, P-LCO, at room temperature and above. In particular, this means that the strain imposed on the epitaxial film by the substrate lattice mismatch “fixes” its spin state very rigidly, preventing it from assuming the pure LS state known from bulk LCO below 35 K and preserving a constant spin-state configuration containing higher spin states (along with LS) for all temperatures studied.

B. Co L edge

The temperature-dependent Co $L_{2,3}$ spectra of the $LaCoO_3$ samples are shown in Fig. 3 for the E-LCO film and in Fig. 4 for the P-LCO film. The spectra correspond in first order to transitions of the type $Co\ 2p^63d^n \rightarrow Co\ 2p^53d^{n+1}$ ($n=6$ for Co^{3+}). They consist of two manifolds of multiplets situated around 780 (L_3) and 795 eV (L_2) and separated by the spin-orbit splitting of the Co $2p$ level. For the P-LCO films of Fig. 4, a small spectral Co^{2+} contribution centered around 777 eV (*cf.* lower panel in Fig. 3) was subtracted. Although this Co^{2+} contribution had been minimized by optimizing growth conditions it could not be completely avoided and might be due to some residual oxygen deficiency.

For the P-LCO films, spectral changes with temperature are obvious: While for 50 K, the spectrum exhibits a pronounced shoulder at about 781.5 eV and a high ratio between maximum and shoulder at the L_2 edge, both features are considerably reduced for the spectra at higher temperatures. It is known that for bulk $LaCoO_3$ [22], the shape of the Co $L_{2,3}$ edge changes with temperature, reflecting the spin-state transition occurring in bulk material. The P-LCO spectra of Fig. 4 are similar to the earlier results of Ref. [22], and the changes observed are, thus, indicative of an analogous spin-state transition from a predominantly LS state at 50 K to a state with increas-

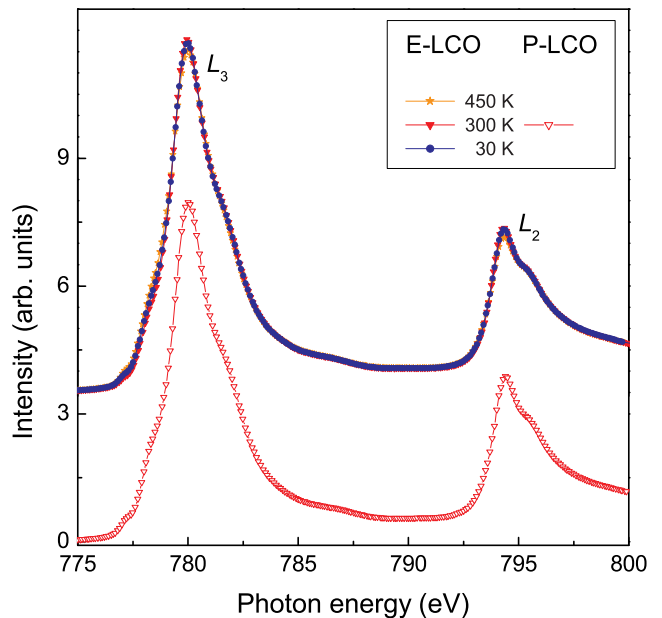


Figure 3: (color online) Upper panel: Co $L_{2,3}$ NEXAFS taken at different temperatures for E-LCO. No discernible spectral changes occur with temperature. Lower panel: Co $L_{2,3}$ NEXAFS for P-LCO at 300 K. This trace is remarkably similar to the E-LCO spectra of the upper panel. (For clarity, the P-LCO 300 K data in the lower panel are offset from the temperature-dependent E-LCO spectra in the upper panel.)

ing admixture of higher spin states at 300 and 450 K. P-LCO is semiconducting, and it turned out impossible to measure this sample at temperatures below 50 K due to strong charging effects. The conductivity might further be reduced for low temperatures by the increasing fraction of Co ions in the LS state.

In order to obtain a more quantitative idea of the temperature-dependent spin-state fractions the P-LCO spectra were modeled by atomic multiplet calculations. The code developed by B. T. Thole [26, 27, 28] and maintained and further developed by F. M. F. de Groot [24, 29] was used to calculate spectra for Co^{3+} in O_h symmetry for different values of the crystal field splitting Δ_{CF} and of the charge transfer energy Δ_c . Charge transfer effects were included by admixing transitions of the type $2p^63d^7\bar{L} \rightarrow 2p^53d^8\bar{L}$, where \bar{L} denotes a hole in the oxygen ligand. Remarkable seems the fact that the ground state has IS character only if the spin-orbit coupling of the $3d$ levels is switched off in the calculations, which in turn means that the IS lies about 0.1 eV in energy higher than the LS and HS levels at their crossing point (at $\Delta_{CF} \approx 1.7$ eV). This implies that it is also not possible to populate the IS state by temperature, at least not in the range reached by our experiments. Although the present calculations and those of Ref. [16] are somewhat different and differ in resulting details, this is an aspect where both agree. Calculations similar to ours have been performed in Ref. [30], and the authors find the HS/LS crossing point at $\Delta_{CF} \approx 2.1$ eV. Our energy scale

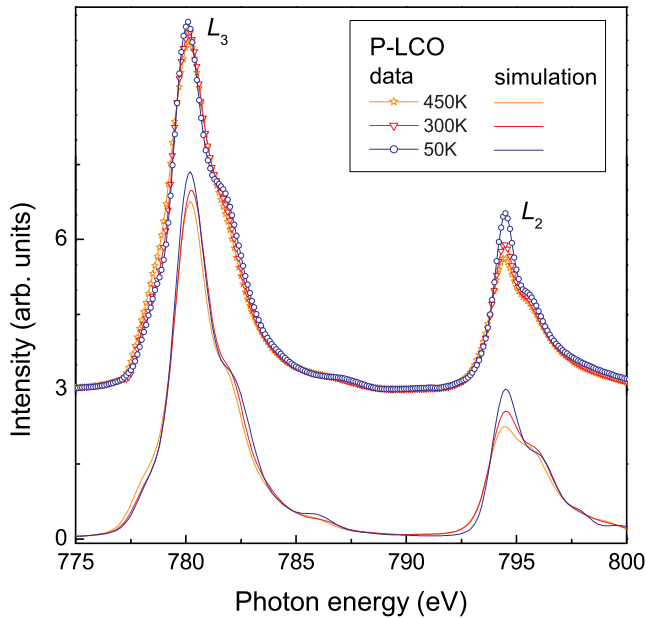


Figure 4: (color online) Co $L_{2,3}$ NEXAFS taken on P-LCO films (upper panel). Spectral background and a small spectral Co^{2+} contribution centered around 777 eV (*cf.* lower panel in Fig. 3) were subtracted. The spectrum taken at 50 K exhibits two important changes over the other spectra: a pronounced shoulder at about 781.5 eV and a significantly higher ratio between maximum and shoulder at the L_2 edge. Lower panel: Atomic multiplet simulations using a mixture of LS and HS spectra. The spectra of the upper panel are well described by the choice of parameters.

is shifted to lower values compared to those calculations by the inclusion of charge-transfer effects [24].

The temperature-dependent spectra of the P-LCO sample were modeled using different ratios of Co^{3+} HS and LS spectra. For the reason just pointed out the IS state does not contribute in the present simulations. Nevertheless, we do not have direct and unambiguous experimental evidence for or against IS or HS in the spectra and, thus, will continue to address non-LS states inclusively as “higher” spin states. Fig. 4 shows the fit results (lines) compared to the data (symbols). The simulations describe the measured spectra very nicely in many details, especially regarding the peak-to-shoulder ratio at the L_2 edge which appears to be very sensitive to the amount of higher spin states in the sample.

The concentration of the LS Co^{3+} extracted from our fits is shown in Fig. 5 (triangles) and compared to the concentrations extracted in Ref. [16] from single-crystal data. Our LS values are lower by about 10 % than the results obtained for the single crystal, which might reflect grain-boundary or residual strain effects of the polycrystalline material. However, we find the same temperature-dependent development of the LS concentration.

For E-LCO, the situation is again very different from P-LCO: Only very little changes with temperature are detectable in Fig. 3, like the absolute amplitude for both the

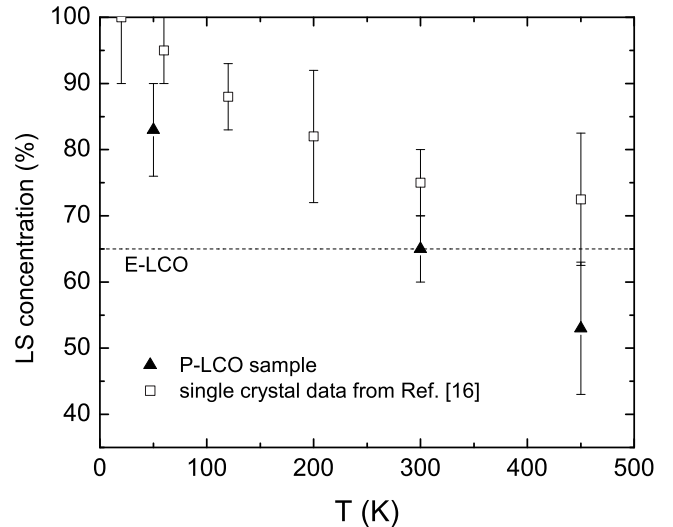


Figure 5: Fraction of Co^{3+} LS as extracted from the multiplet simulations of the NEXAFS spectra for P-LCO, compared with results from Ref. [16] for single-crystalline LCO. The E-LCO spectra are very similar to the P-LCO result at 300 K, and the corresponding LS fraction is included as a dashed line.

L_3 and L_2 peaks. These small changes can be explained by an increased phonon broadening at higher temperatures. The shape of the spectra taken at all temperatures is very similar to that of P-LCO at 300 K — see also the comparison between upper and lower panels in Fig. 3. The constant spectral shape means, in particular, that no spin-state changes are visible. This agrees perfectly with the observations made at the oxygen edge. It also shows, *cf.* Fig. 5, that for E-LCO at low temperature the amount of Co^{3+} in the LS state is significantly lower than at similar temperatures in P-LCO. A low LS population and, conversely, a significant population in higher spin states is clearly a necessary prerequisite for ferromagnetism.

It remains to be clarified why higher spin states are more abundant in E-LCO at low temperature. We observe that, in contrast to the largely relaxed structural state of P-LCO, the LSAT substrate imposes strain on E-LCO, leading, among other things, to an increased unit-cell volume (56 \AA^3 versus 54 \AA^3 for E-LCO and P-LCO, resp.) [17] and to increased a, b lattice parameters (3.87 \AA vs. 3.80 \AA). Geometry indicates that this will result in a reduced tilt of the CoO_6 octahedra in LaCoO_3 [18]. This, in turn, enhances the overlap of the e_g -symmetry $3d$ orbitals with the O $2p$ orbitals, whereas the hybridization of the t_{2g} states with the O $2p$ orbitals is reduced. Density functional calculations [31] demonstrate a resulting stabilization of the higher spin states; this is also consistent with the larger ionic radius of the Co^{3+} ions in IS and HS [32].

IV. SUMMARY AND CONCLUSIONS

Both O *K* and Co *L*_{2,3} NEXAFS results clearly demonstrate that for E-LCO thin films grown on LSAT, a significant and temperature-independent fraction of higher spin states is present. This is a necessary prerequisite for ferromagnetism and, thus, helps to explain the magnetic behavior of E-LCO. In contrast, P-LCO exhibits temperature-dependent spin-state transitions in analogy to bulk LCO, resulting in a very high LS population at low temperature and, thus, paramagnetic behavior.

Acknowledgments

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